

Grazing Angle IR Microscopic Study on Phosphate Adsorption on the Surfaces of Hematite Single Crystal.

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Introduction: Phosphate is the prime cause of water quality degradation in agricultural watersheds. Surface runoff of dissolved and particulate phosphorus from soils is a major pathway for discharge of phosphorus into surface waters. Phosphate adsorption mechanisms on iron oxides are essential for understanding the bioavailability and fate of soil phosphorus. The distribution of phosphate between solid and solution phases is controlled by the composition and structures of P associated with Fe oxides. The surfaces of the minerals are heterogeneous and different crystal surfaces may have different reactivities toward adsorbed species. However, previous macroscopic and spectroscopic observations of polycrystalline samples cannot resolve reactions occurring at different surfaces of each mineral. The observed phenomena are actually the sum of the reactions on different surfaces. Depending on the methods used to observe the reaction, different conclusions on the adsorption mechanisms of phosphate have been obtained [1, 2]. To determine the structural configurations of adsorbed phosphates on different crystal surfaces of hematite ($\alpha\text{-Fe}_2\text{O}_3$), which is abundant in soils, grazing angle IR microscopy was conducted for phosphate adsorption on the surfaces of hematite single crystal. Because single crystal specimens have at least one dimension > 0.1 mm, the orientations of the crystals can be changed for spectroscopic measurements. With the grazing angle method, the incident angle of the IR beam to sample surfaces is 85 degree and IR spectra are obtained by the reflected radiation from the surfaces. The absorption for IR radiation with grazing angle incidence is 5000 times greater than that at normal incidence [3]. Therefore, this technique is useful for obtaining the spectra of a layer of adsorbed species on surfaces.

Methods and Materials: The surfaces of the single crystal specimens of hematite were determined using X-ray diffraction and then were abraded and polished using $0.1\ \mu\text{m}$ diamond colloids. The polished crystals were then transferred onto glass slides and the selected surfaces were set parallel to the glass slides. To enhance the spectroscopic sensitivity to the adsorbed species and to compress the contributions of the signals from the bulk solids, grazing angle IR microscopy was used to obtain the reflection spectra after $0.05\ \text{mL}$ $10\ \text{mM}$ KH_2PO_4 solution was added and dried on the polished surfaces.

Results: Our preliminary studies for hematite surfaces showed that the grazing angle IR spectroscopy is feasible with polished mineral surfaces. As shown in the Figure 1, the reflection spectrum of phosphate precipitated on hematite 012 face at pH 4 exhibits two bands at 1073 and $1032\ \text{cm}^{-1}$. These values are close to those (i.e., 1082 and $1020\ \text{cm}^{-1}$) measured for adsorbed phosphate on polycrystalline hematite in the same region using *in-situ* ATR-FTIR spectroscopy. These two bands correspond to P-OFe and P-O bonds that are perpendicular to the surface. Our further experiments will focus on increasing the spectral quality (S/N ratio and resolution) of the reflection spectra and obtain spectra on different crystal surfaces as a function of adsorbed phosphate concentration and pH.

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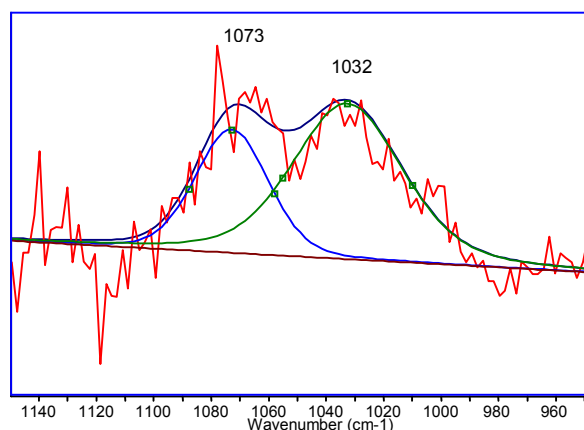


Figure 1. Grazing angle IR spectrum of phosphate on hematite 012 surface.